

"Molecular and Nanostructured Materials for Solar Photovoltaics"

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University of Pennsylvania

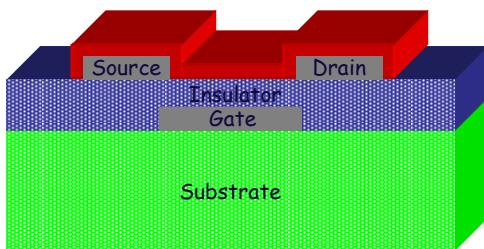
Electrical and Systems Engineering Department
Materials Science and Engineering Department

Brookhaven National Lab
May 20, 2008

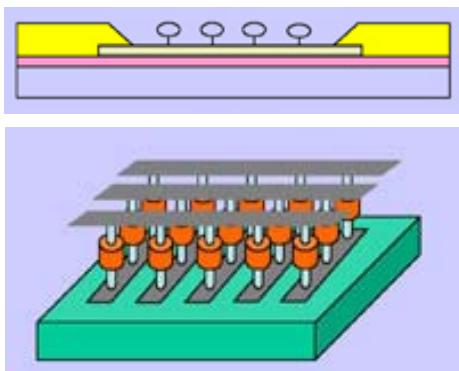


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Molecular and Nanoscale Materials and Devices



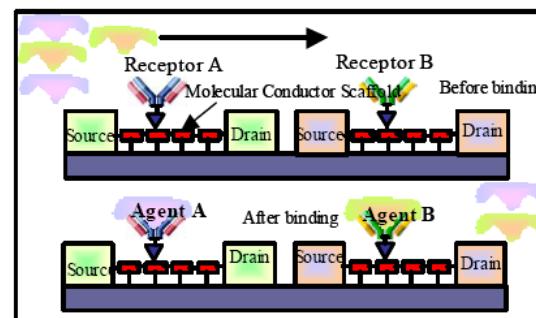
Transistors



Memory

Fundamental Understanding
Of the Chemistry and Physics

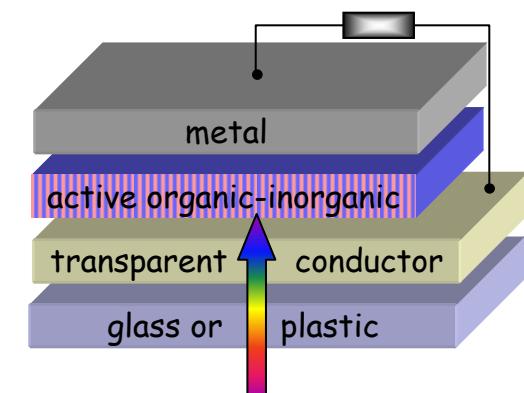
Charge Transport
Photoluminescence
Switching (RedOx, Conformational)
Charge Generation/Separation
Molecular Recognition



Sensors



Light Emitting Diodes



Photovoltaics



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Low-cost and Flexible Macroelectronics

Molecular and Nanoscale Materials - Low temperature, solution-based processing

Alternatives



Displays



Smartcards



RFID Tags

Flexible



Enabler

e-paper

Signs

Diary

Books

Textiles



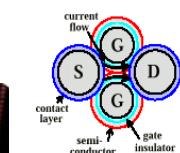
Form Factor



Widespread Adoption
Form Factor



Poly IC



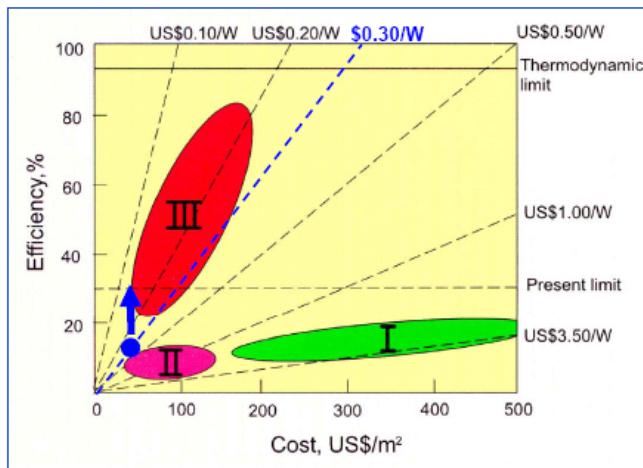
Bundle

Solomon, Shaw, Kagan,
Dimitrakopoulos, Ning
US 6 437 422



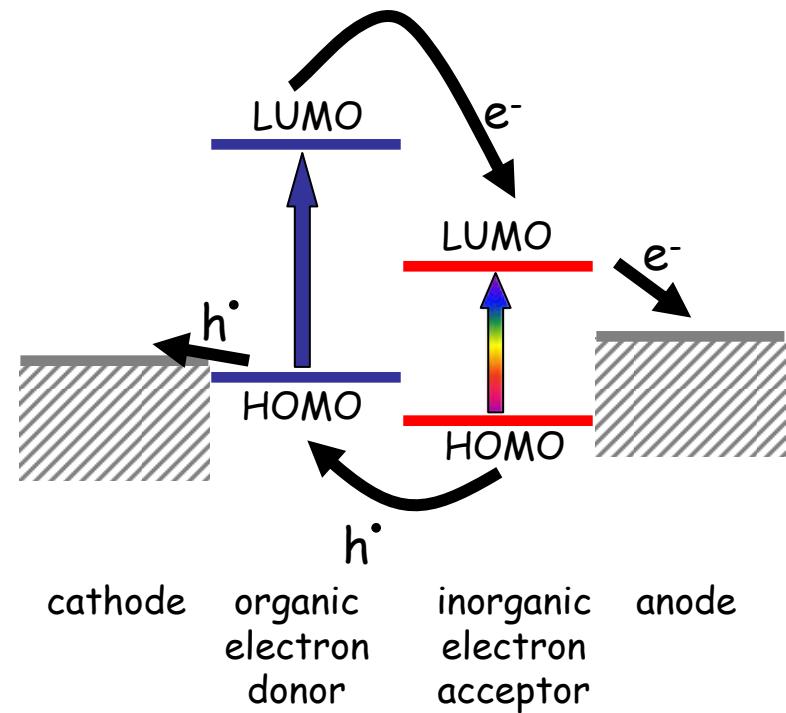
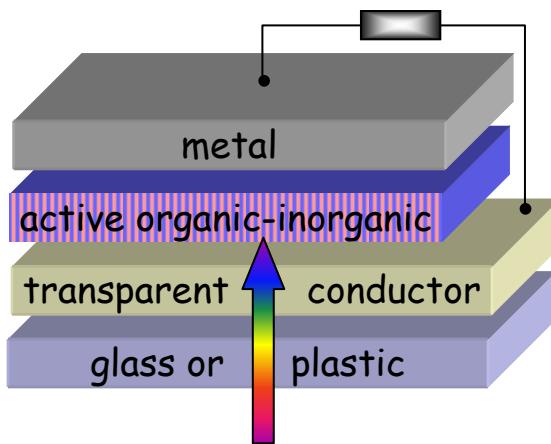
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Engineering Molecular and Nanostructured Materials for Low-Cost, High-Performance Solar Cells



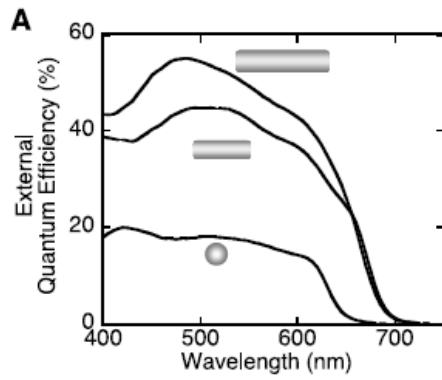
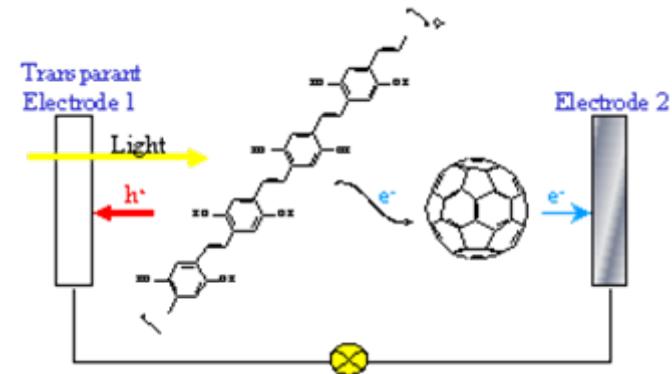
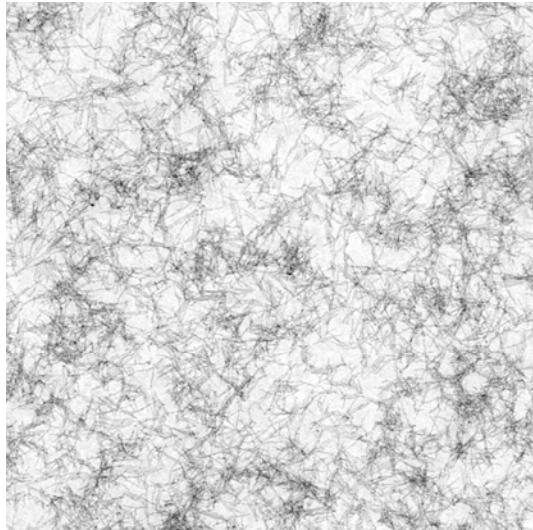
Costs are modules per peak W; installed is \$5-10/W; \$0.35-\$1.5/kW-hr

M. Green (UNSW)



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Organic-Inorganic Hybrid Photovoltaics



A. P. Alivisatos group

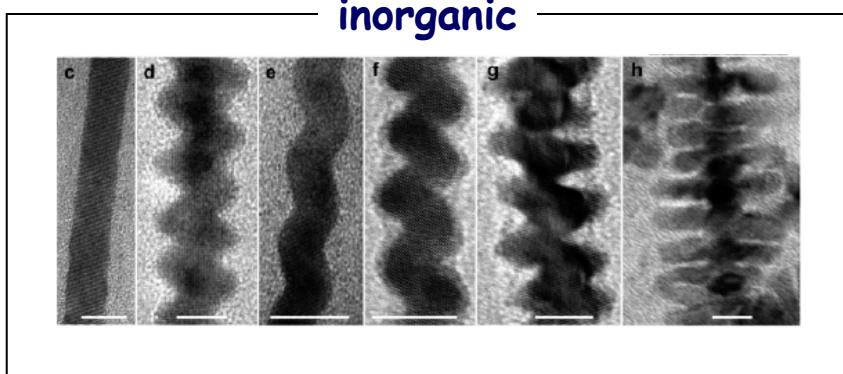
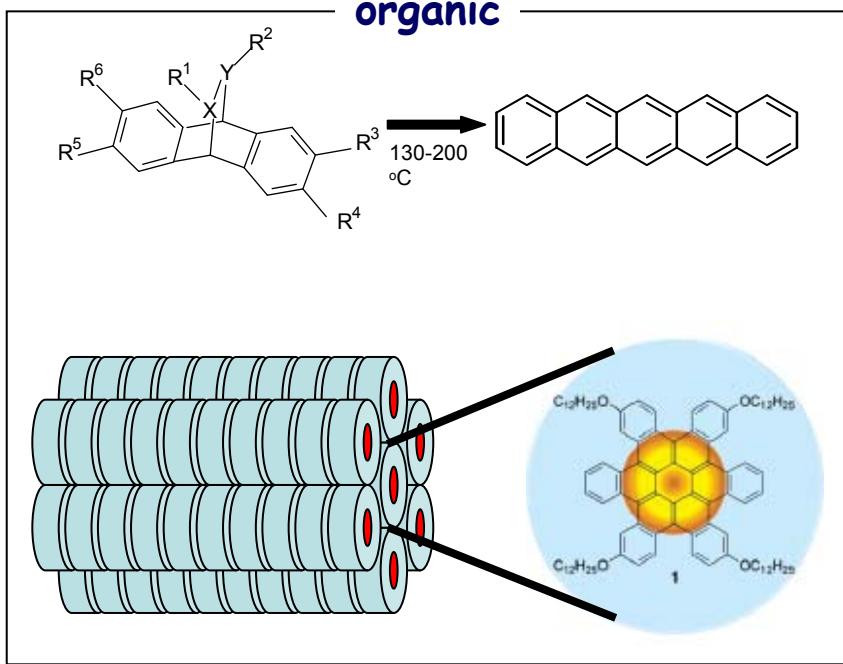


Konarka



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Organic-Inorganic Hybrid Photovoltaics

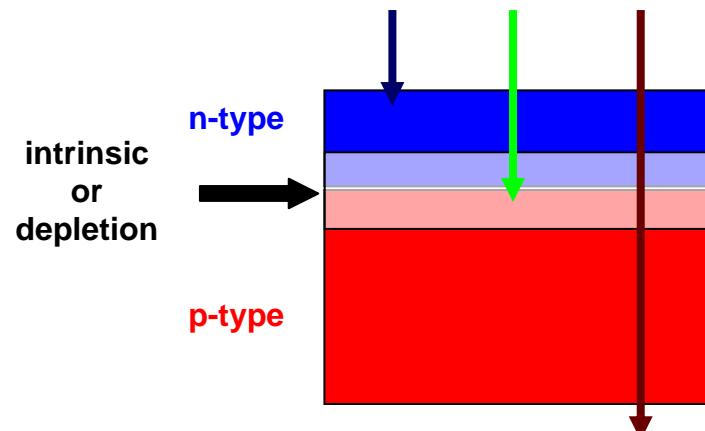


- Maximize spectral sensitivity with high optical density materials
 - Tailor chemistry to control morphology to make 3D heterostructures where n and p-type materials are within the exciton diffusion length
 - Provide driving force for charge separation
 - Control reaction rates to prevent interfacial recombination losses
 - Provide high mobility n- and p-type conduits for charge transport
 - Engineering device interfaces
 - Stable and environmentally friendly materials and processes
-
- Fabrication and Characterization of high performance solar cells by low-cost methods on rigid and flexible substrates

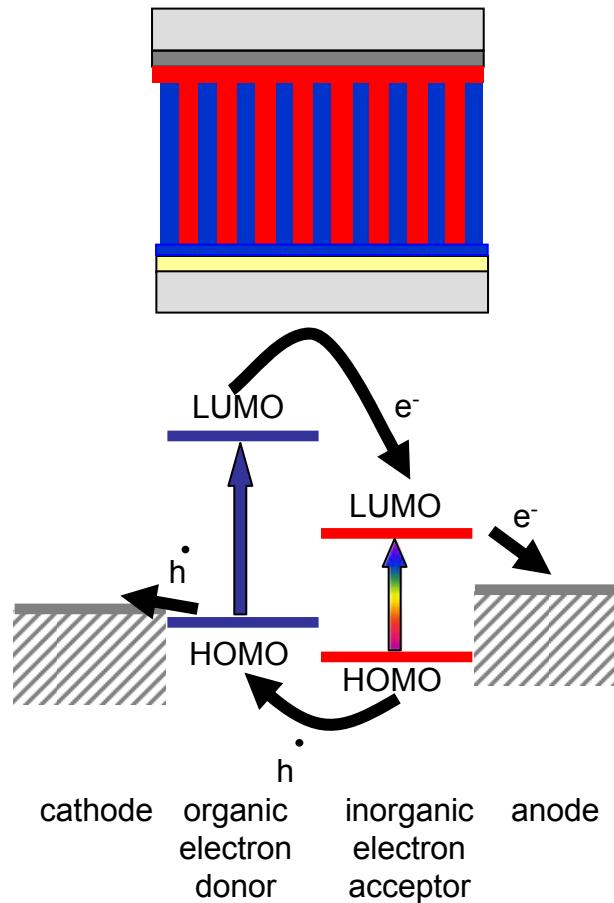
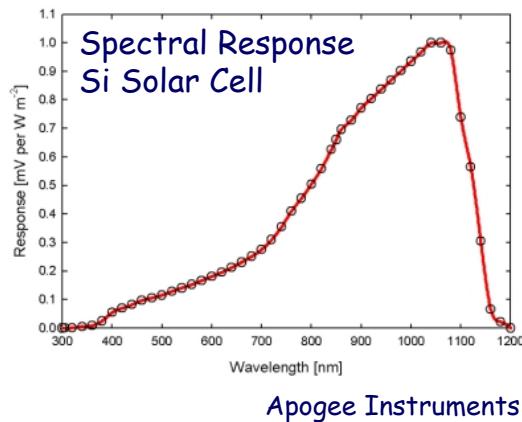


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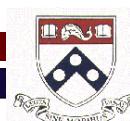
Planar versus 3D Interpenetrating PN Heterojunctions



- Photons within a diffusion length of the depletion region are separated and collected
- Open circuit voltage defined by energy gap and doping level

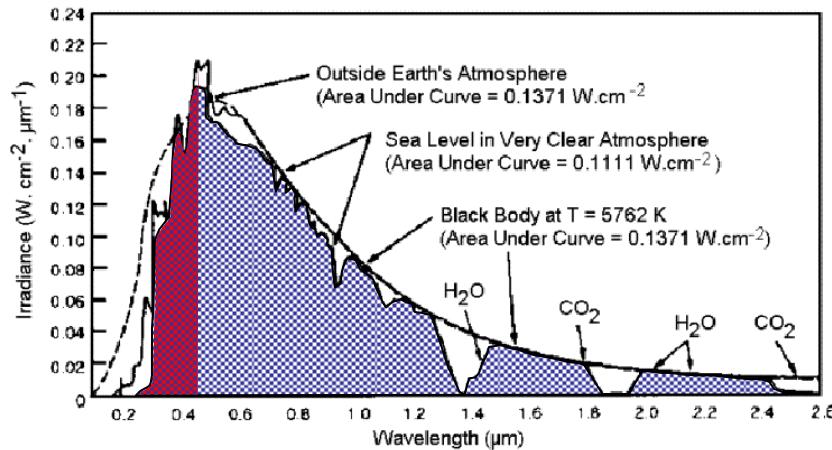


- Structure materials on the length scale of the exciton diffusion length (5-10 nm)
- Separate bound excitons in organics and nanostructured materials
- V_{oc} defined by $n_{LUMO} - \rho_{HOMO}$ and losses at electrodes

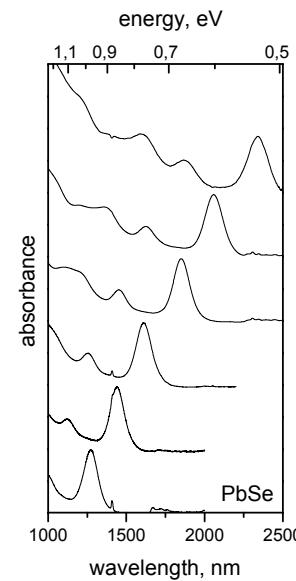
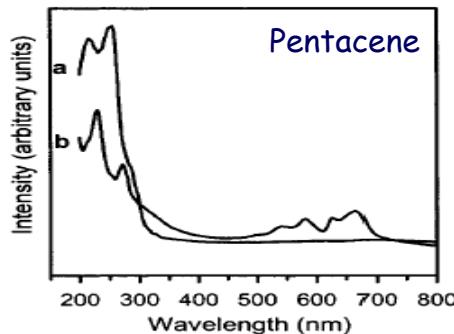


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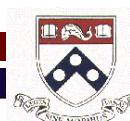
Maximizing Collection of the Solar Spectrum



Pentacene and PbSe QD Absorption Spectra

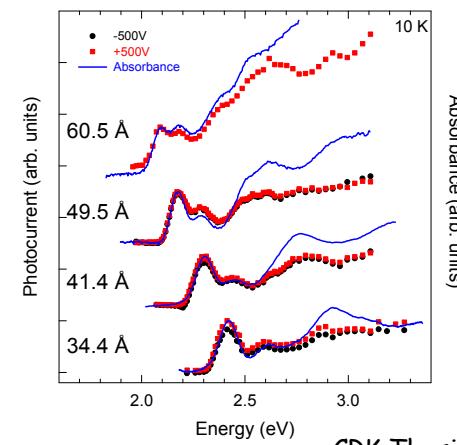
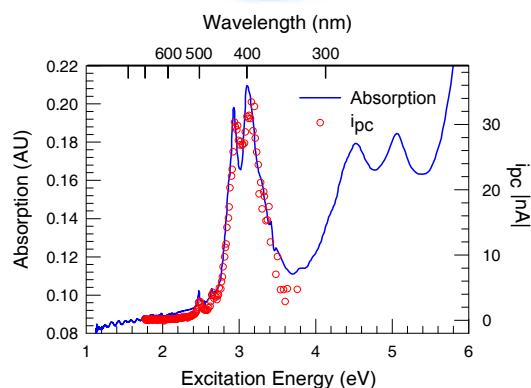
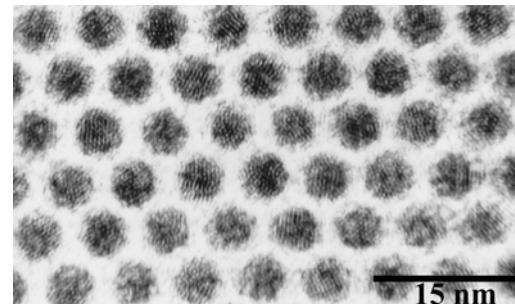


Quantum confined nanostructures have molar absorption coefficients similar to molecules
BUT It's the absorption/volume that matters
Red absorbing organic compounds are important

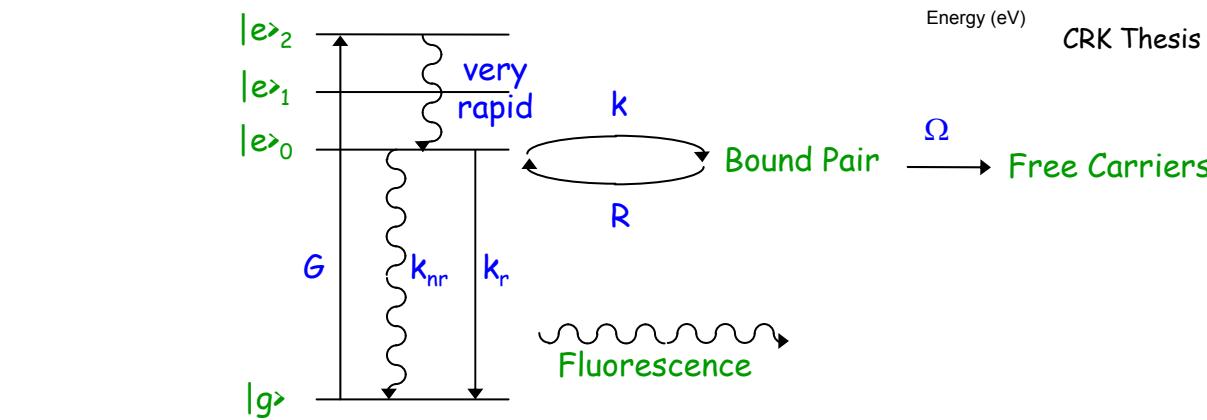


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Exciton Separation in Organic and Nanoscale Materials

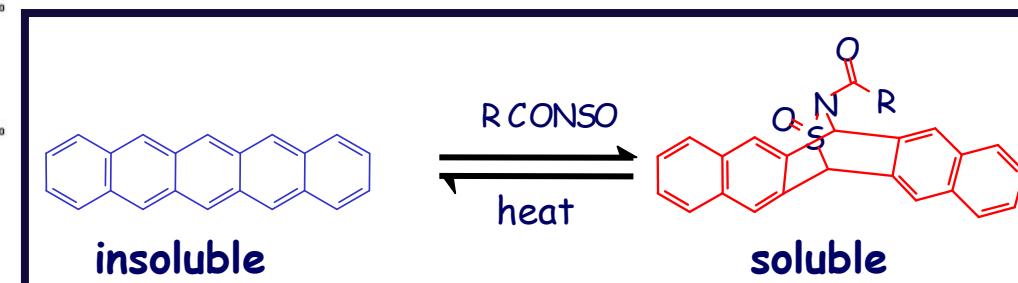
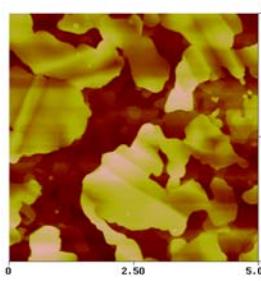


CRK Thesis

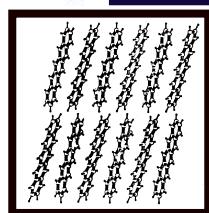


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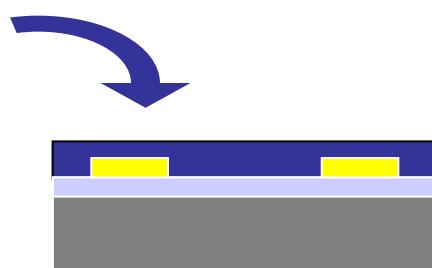
Solution-Processable Organic Semiconductors: Pentacene



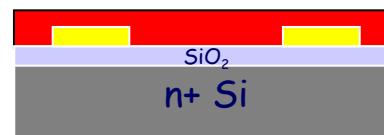
Tailor R to affect:
solubility and photosensitivity



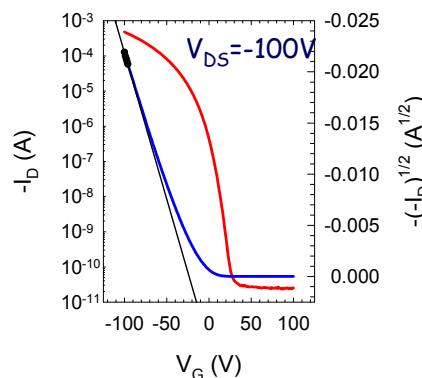
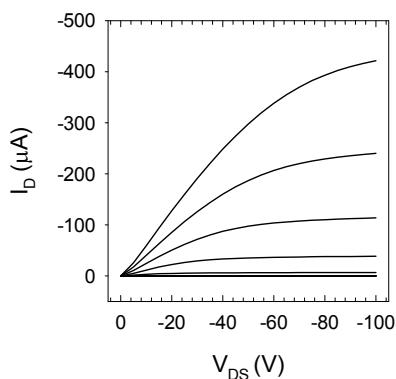
Transport
Direction



heat in N_2
 $120-200^\circ C$



spin-coat
precursor
in air



$$\mu \sim 0.5-1 \text{ cm}^2/\text{V}\cdot\text{sec}$$
$$I_{ON}/I_{OFF} \sim 10^7$$

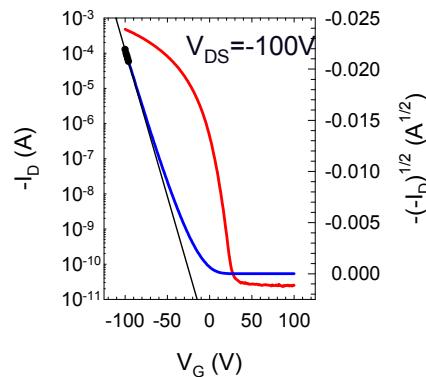
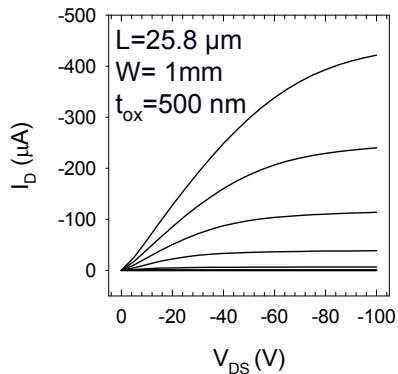
"Current Induced Chemistry"
Environmental and
operational stability

A. Afzali, C. D. Dimitrakopoulos, T. L. Breen, JACS, 124, 8812 (2002).
C. R. Kagan, A. Afzali, T. O. Graham, Appl. Phys. Lett. 86, 193505 (2005).



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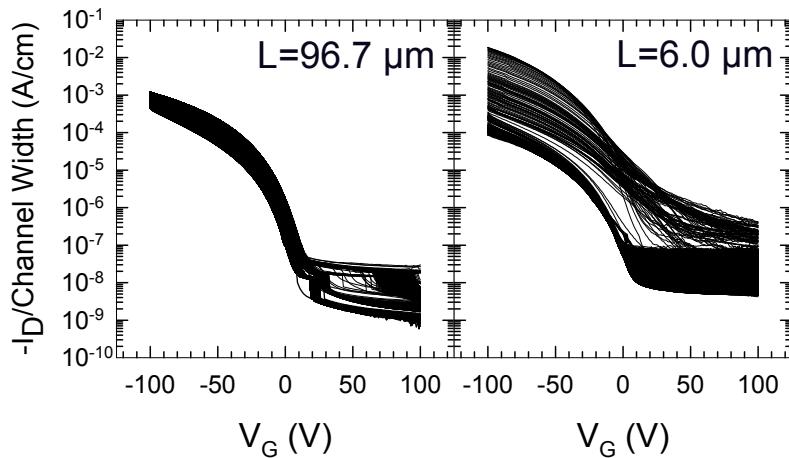
Environmental and Operational Influences on Charge Transport in Pentacene



$$\mu \sim 0.5-1 \text{ cm}^2/\text{V}\cdot\text{sec}$$
$$I_{ON}/I_{OFF} \sim 10^7$$



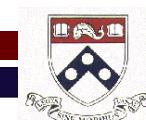
Cycle $I_D - V_G$ 10001x



Decreasing Channel Length

- higher current density
- faster decrease in I_{ON}
- faster increase in I_{OFF}
- more dramatic shift in V_{th}

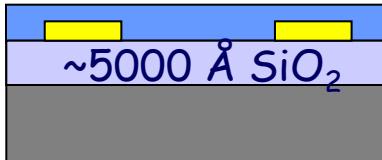
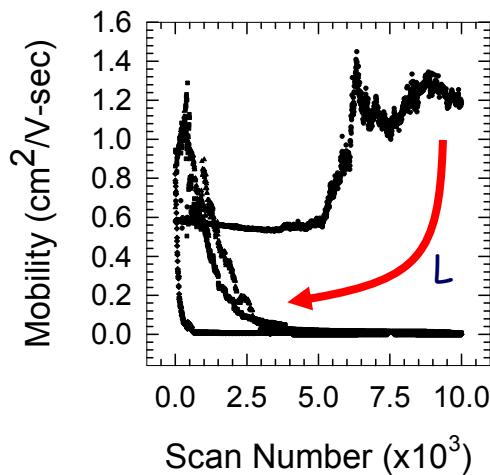
C. R. Kagan, A. Afzali, T. O. Graham, Appl. Phys. Lett. 86, 193505 (2005).



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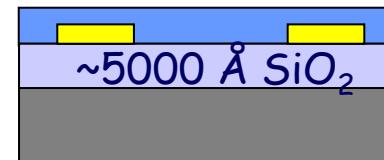
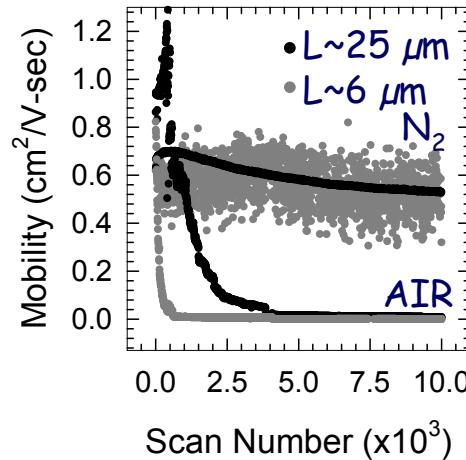
Environmental and Power Dependence on Organic Transistor Stability

In Ambient Air



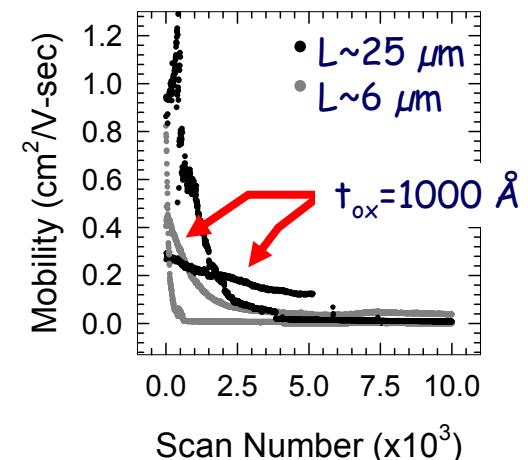
$V_{\text{app}} \sim 100\text{V}$

In Ambient N_2



$V_{\text{app}} \sim 100\text{V}$

Scaled Device in Air



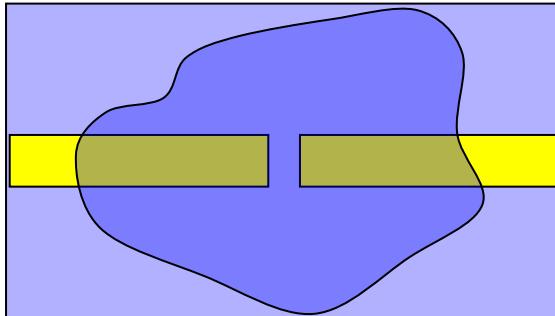
$V_{\text{app}} \sim 30\text{V}$

Degradation via thermal oxidation at high power in ambient air
Encapsulation or Scale Device Geometry for Lower Power Operation

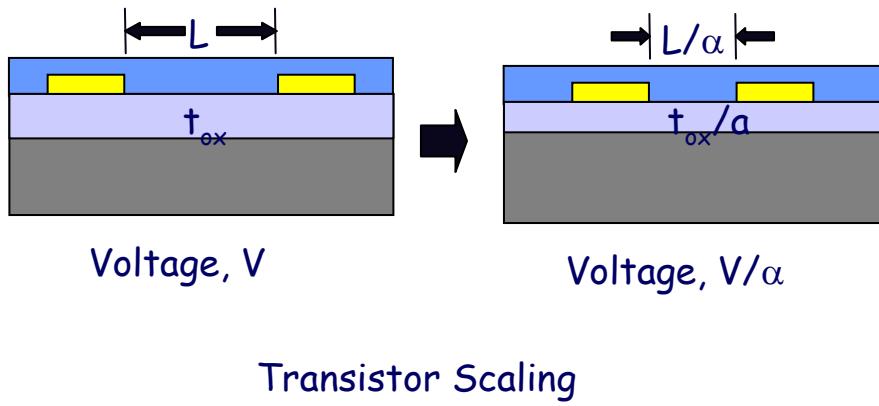


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Nanometer Scale Devices



- Study charge transport in single organic semiconducting grains
- Role of grain boundaries on transport
- Learn about the electrostatics and contacts of highly scaled devices



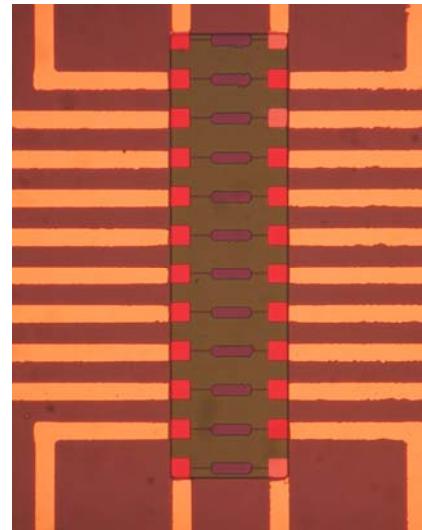
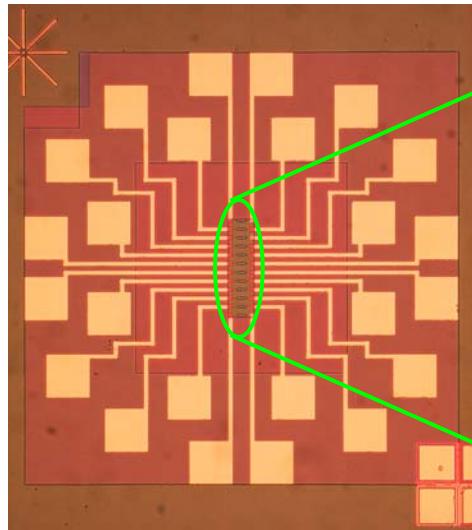
Technologically advantageous

- Lower voltage operation
- Higher speed operation, by α



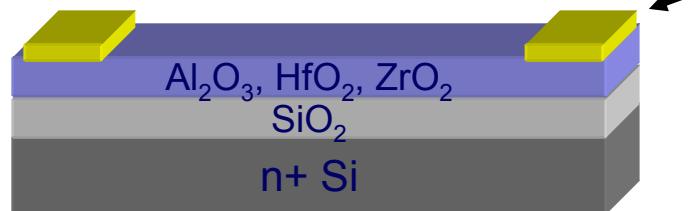
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Fabrication of Nanometer Scale Devices

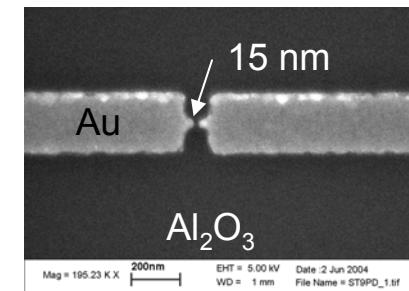
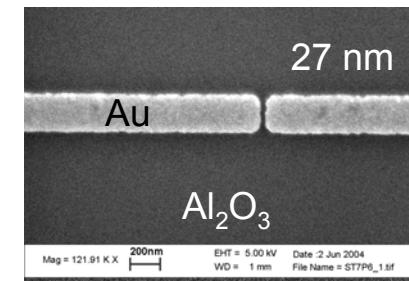
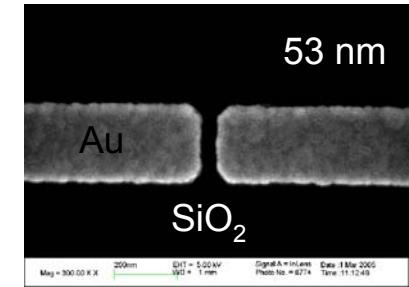


$L \sim 15 \text{ nm} - 100 \text{ nm}$

Dielectric layers used to reduce leakage and isolate channels



Metals
AuPd
Ti/Au
Ti/Pd
Ti/Pt



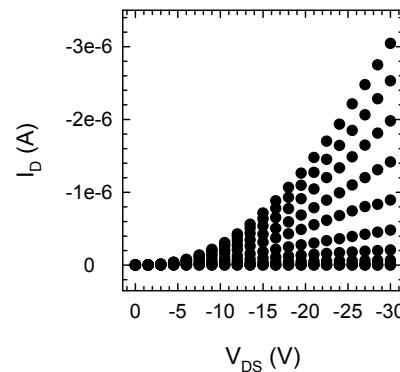
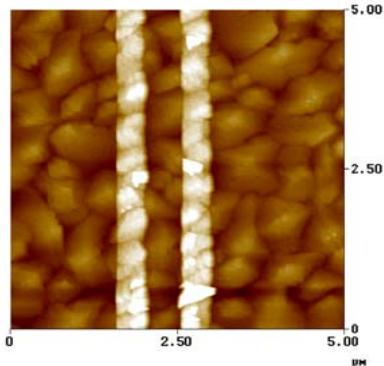
Dielectrics with or without high-k metal oxide



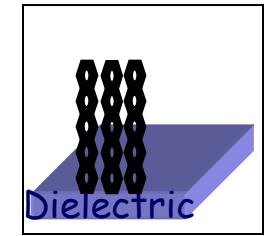
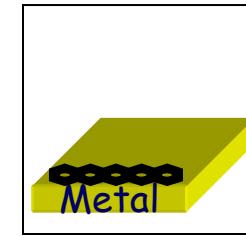
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Nanometer Scale Pentacene Transistors Vacuum vs Solution Deposition

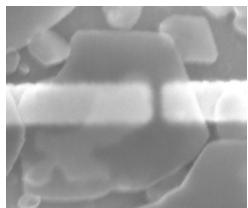
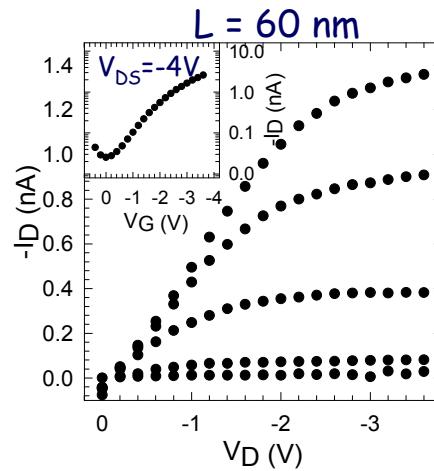
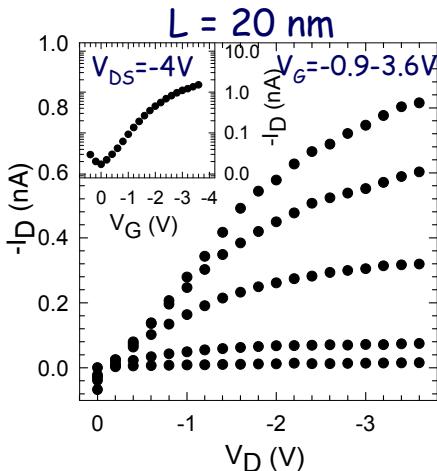
Vacuum Deposited



- grain growth different on metal and dielectric surfaces

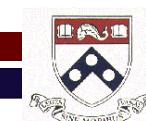


Solution Deposited via Precursor Channel Length < Pentacene Grain Size



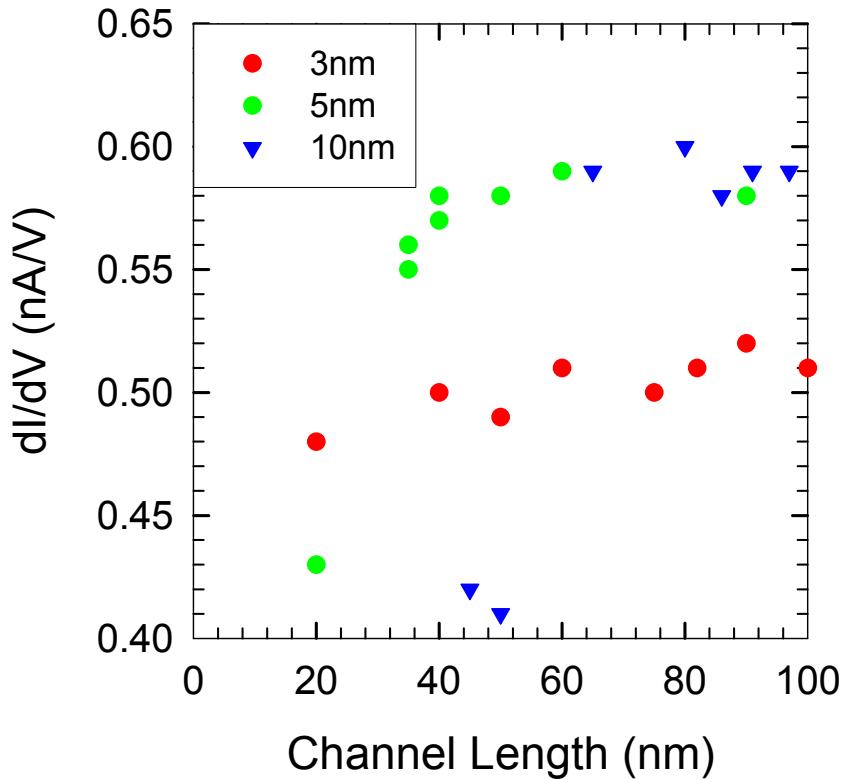
- grains span junctions
- reliably well-behaved characteristics allowing statistics

G. S. Tulevski, A. Afzali, T. O. Graham, C. Nuckolls, C. R. Kagan, Appl Phys Lett, 89, 183101 (2006).

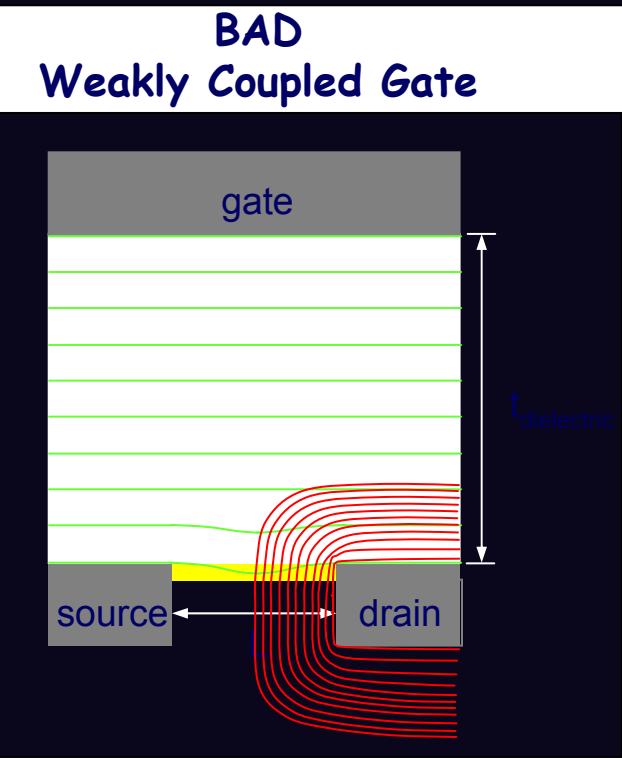
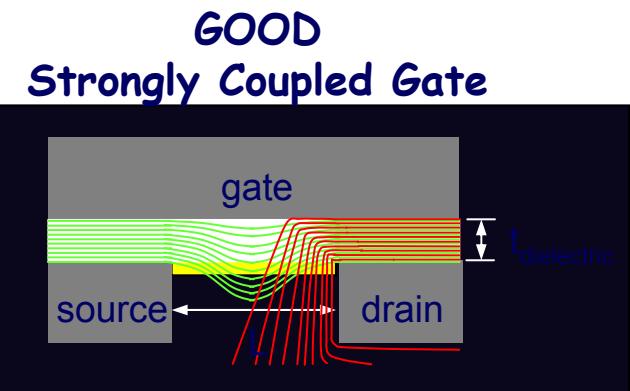


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Device Electrostatics



Good Electrostatics for $L \geq 5 * t_{ox}$

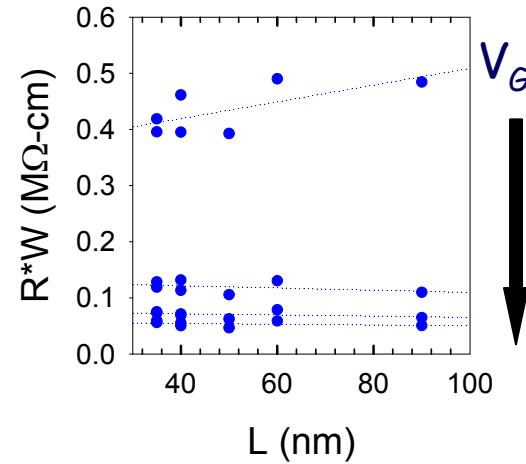
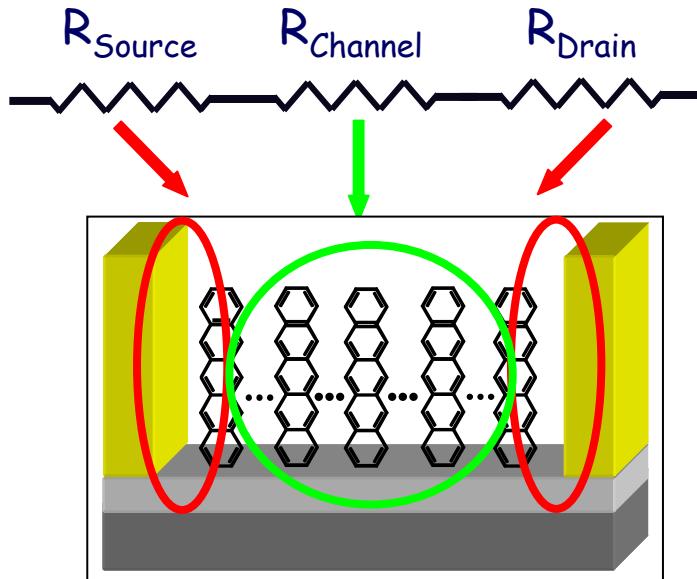


Constant Potential Lines from
Gate and Drain



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Contact Dominated Devices



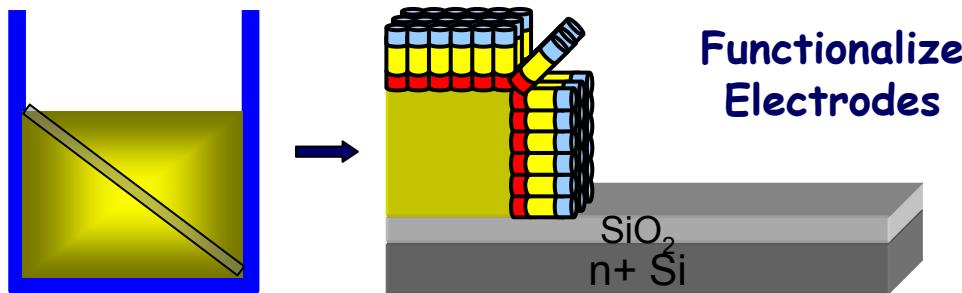
$$R_{\text{Total}} \sim R_{\text{Source}} + R_{\text{Drain}}$$

Contact resistance similar to
that found in μm -scale devices

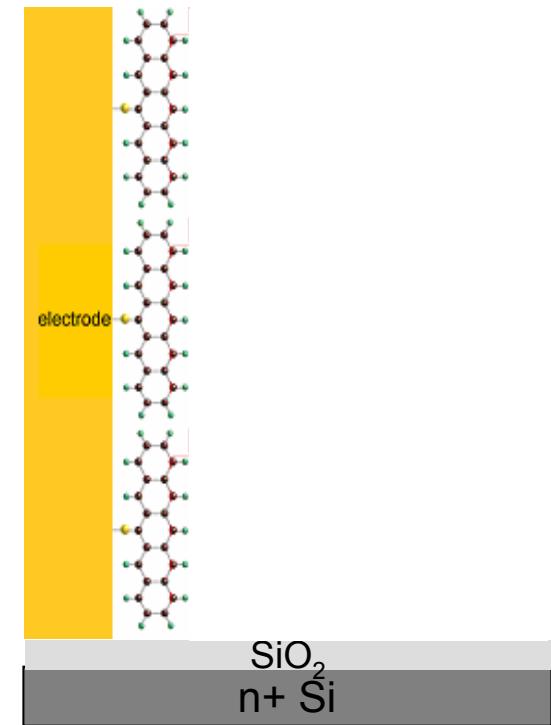
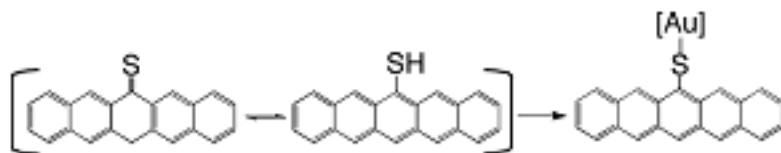
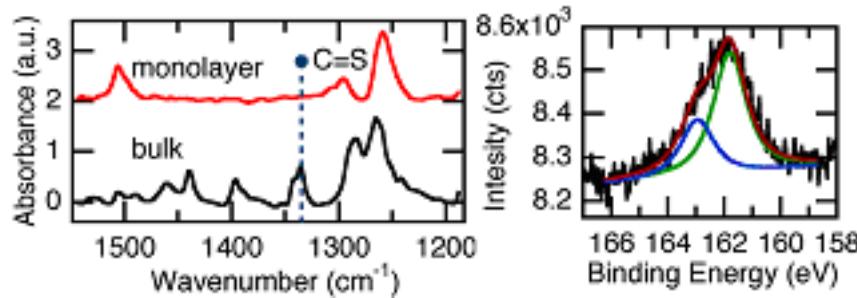


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Engineering Device Interfaces through Molecular Self-Assembly

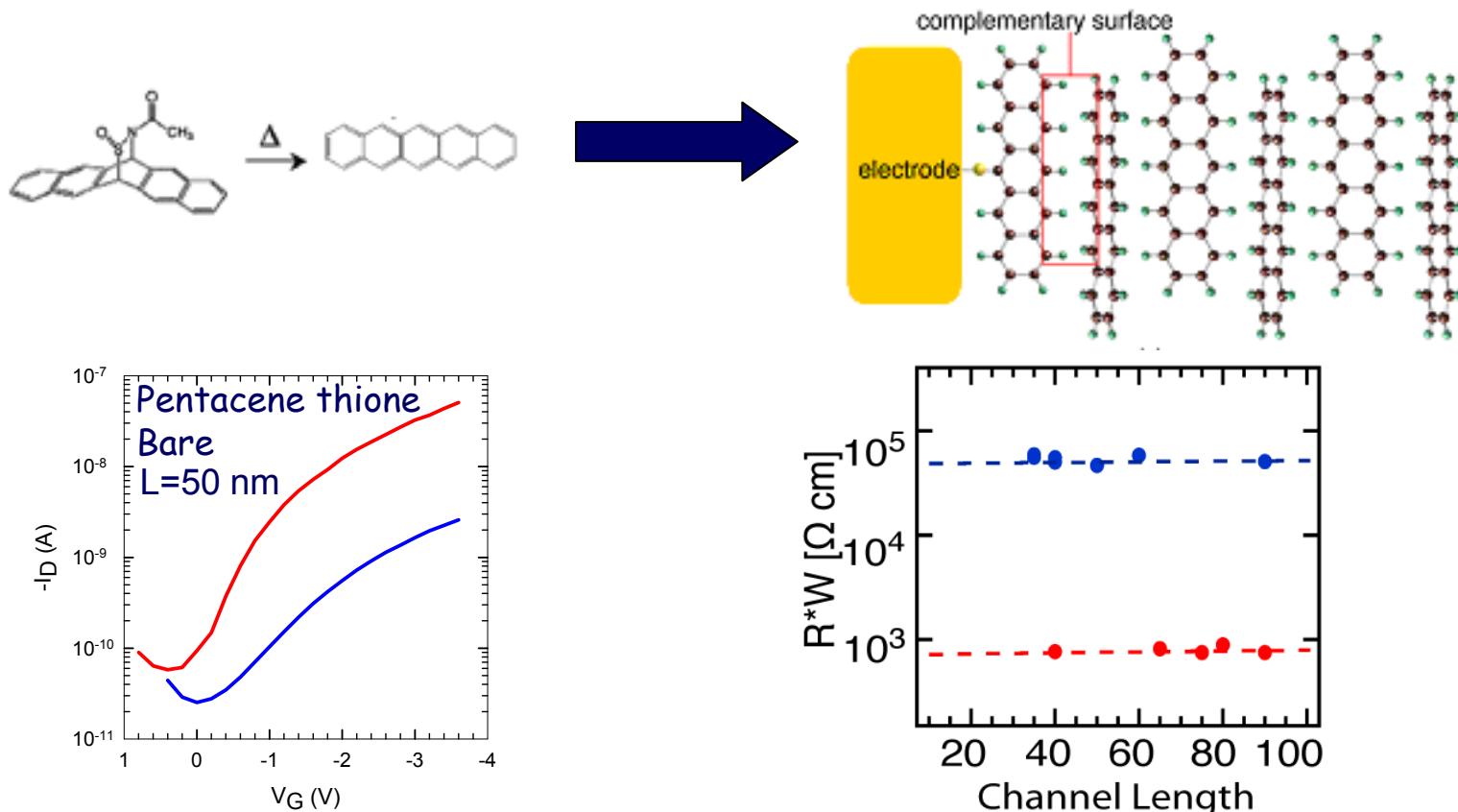


Functionalize
Electrodes



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Chemical Manipulation of the Contacts in Pentacene Transistors



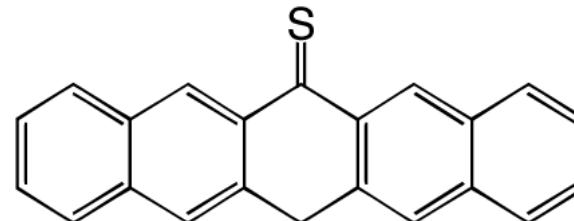
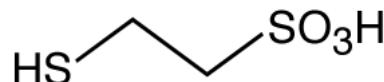
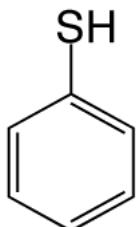
Yield is high (>80%)
Transconductance is 25x
 I_{ON}/I_{OFF} is 80x higher
 R_c 100x lower

G. S. Tulevski, Q. Maio, A. Afzali, T. O. Graham, C. R. Kagan, C. P. Nuckolls, J. Am. Chem. Soc., **128**, 1788 (2006).



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Surface Modification



Device Performance of Modified OFET

Compound	I_{ON}/I_{OFF}	μ^1	g_m^2
None	100	$1.4 \pm 0.3 \times 10^{-4}$	0.5 ± 0.1
1	50	$5.1 \pm 0.9 \times 10^{-4}$	1.3 ± 0.3
2	35	$7.6 \pm 1.1 \times 10^{-4}$	1.8 ± 0.2
3	8000	$2.2 \pm 0.7 \times 10^{-2}$	12.2 ± 1.4

[1] cm²/Vs

[2] nA/V

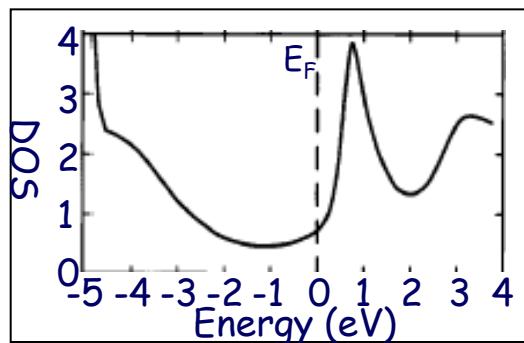
Electronic and structural Similarity is important



Penn

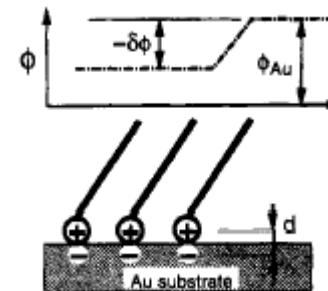
Metal-Molecule Interfaces

Broadening of Molecular Levels at Metal Interface

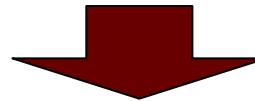


Lang, Avouris, Phys. Rev. B, **64**, 125323 (2001)
Vasquez, Flores, Kahn, IPAP, **6**, 1.

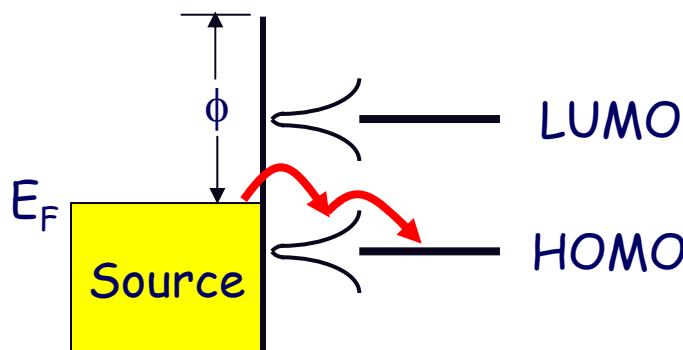
Charge Transfer



Schönenberger et al, J. Phys. Chem. **99**, 3259 (1995)



Modifying Contacts in Large Junctions



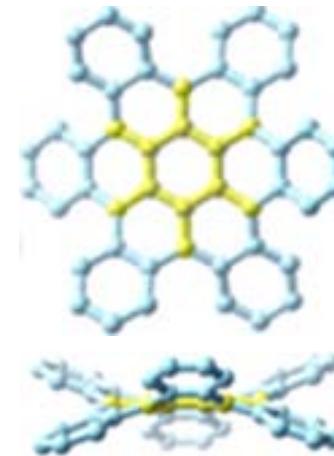
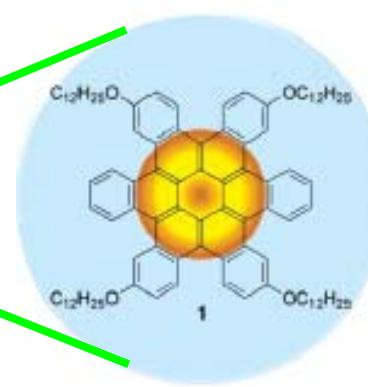
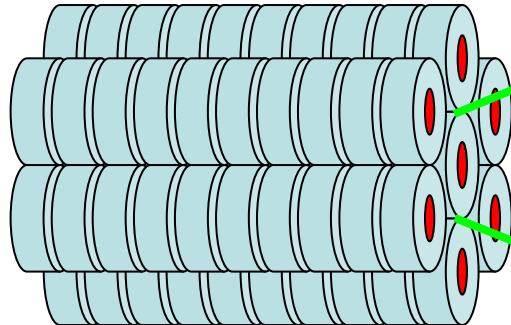
Akin to Grading Junctions

Develop graded junctions in organic and nanostructured materials and devices

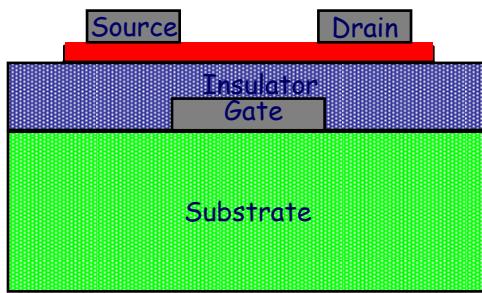


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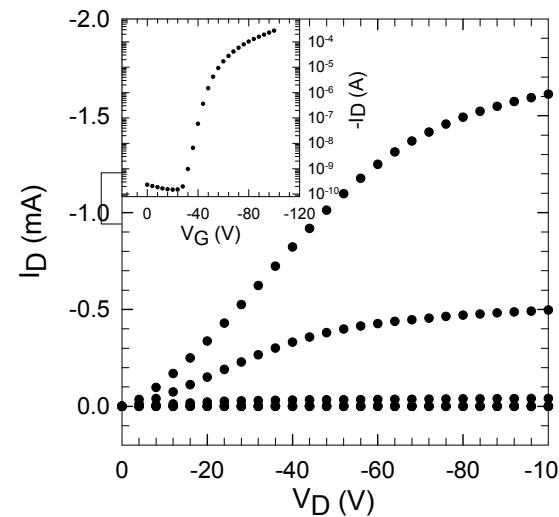
Core-Cladding One Dimensional Photoconductors Molecular Architectures to Control the Flow of Charge and Energy



S. Xiao, M. Myers, Q. Miao, S. Sanaur, K. Pang, M. L. Steigerwald, C. Nuckolls, *Angew. Chem. Int. Ed.* **44**, 2 (2005).

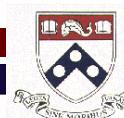


spin-cast from chlorinated solvent
anneal at 150 °C



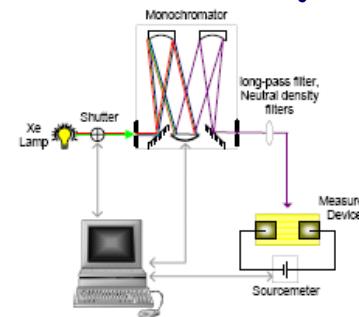
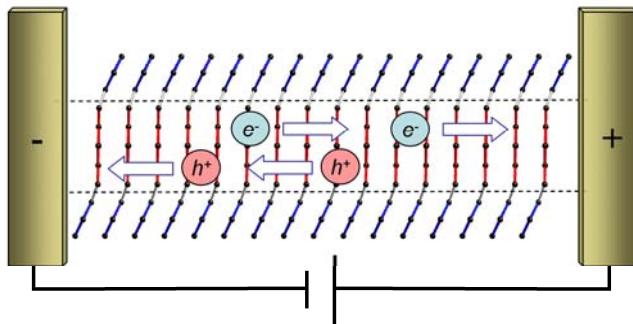
$$\mu \sim 0.09 \text{ cm}^2/\text{V}\cdot\text{sec}$$
$$I_{ON}/I_{OFF} \sim 10^7$$

G. S. Tulevski, C. P. Nuckolls, C. R. Kagan

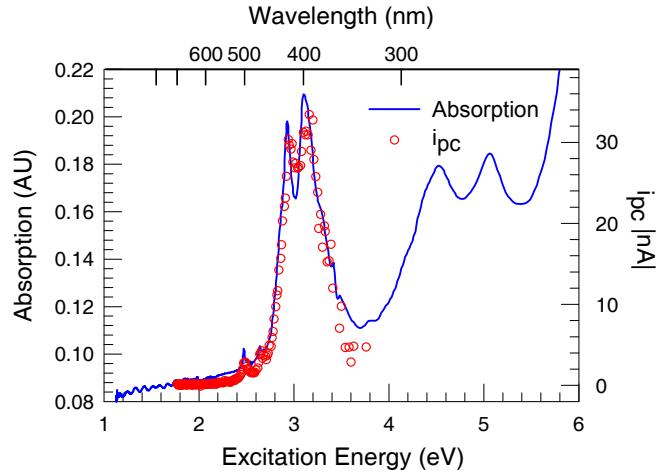


Penn

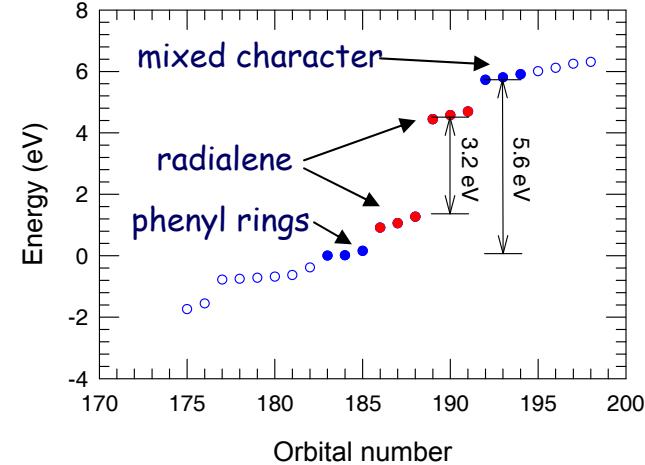
One-Dimensional Photoconductivity



Absorption and Spectral Response



Density Functional Theory



- Excitation rapidly relaxes to lowest energy state prior to separation
- Charge generation efficiency ~ 1 at $E \geq 10^4$ V/cm

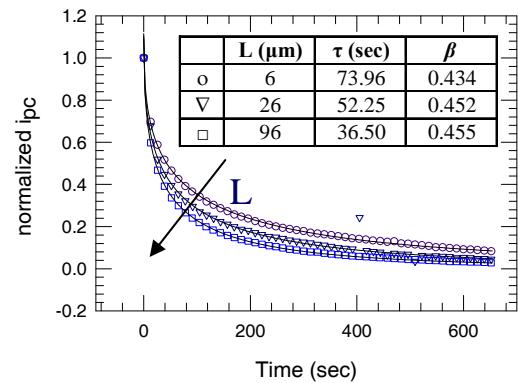
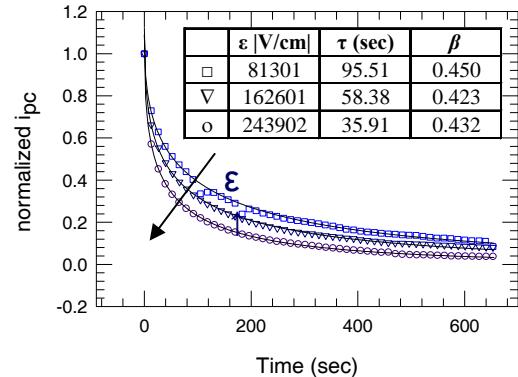
- Low-energy hexaradialene core
- High energy, insulating alkoxyphenyl cladding

Y. S. Cohen, S. Xiao, M. L. Steigerwald, C. Nuckolls, C. R. Kagan, *Nano Lett.* 6, 2838 (2006)



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Persistent Photoconductivity and Intensity Dependence



Fit to stretched exponential

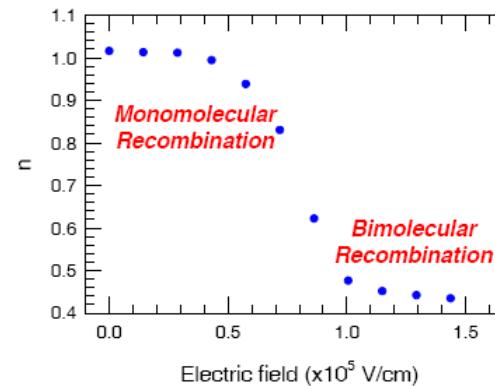
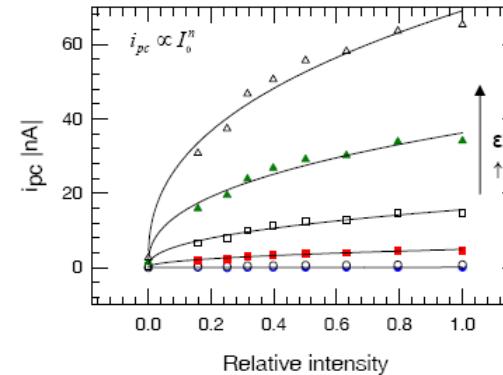
$$i_{pc}(t) = i_0 \exp[-(t/\tau)^\beta]$$

β describes degree of dispersion

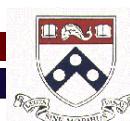
Relationship to dimensionality:

$\beta = 1$ in 3D

$\beta = 0.5$ in 1D



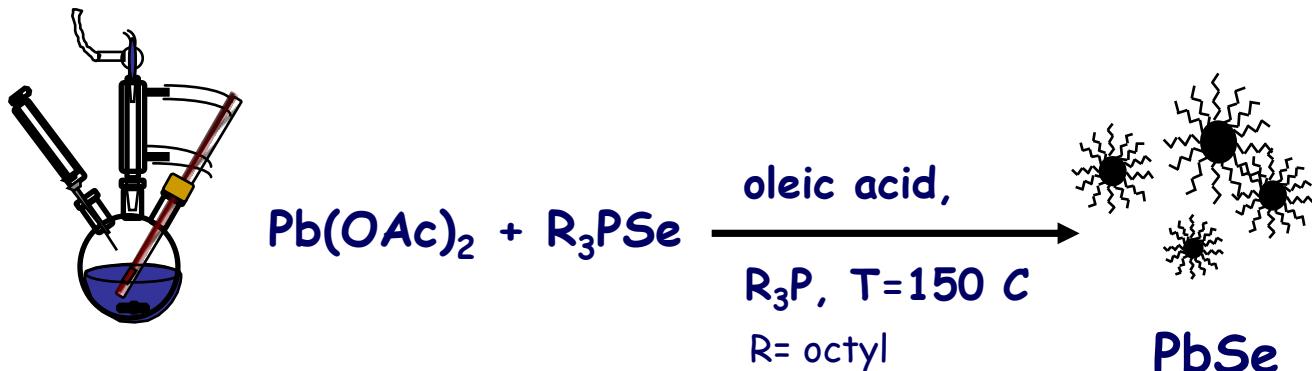
One-dimensional, intracolumnar charge transport
through the radialene core
independent of applied field or channel length



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Synthesis of PbSe Nanocrystals and Nanowires

Synthesis

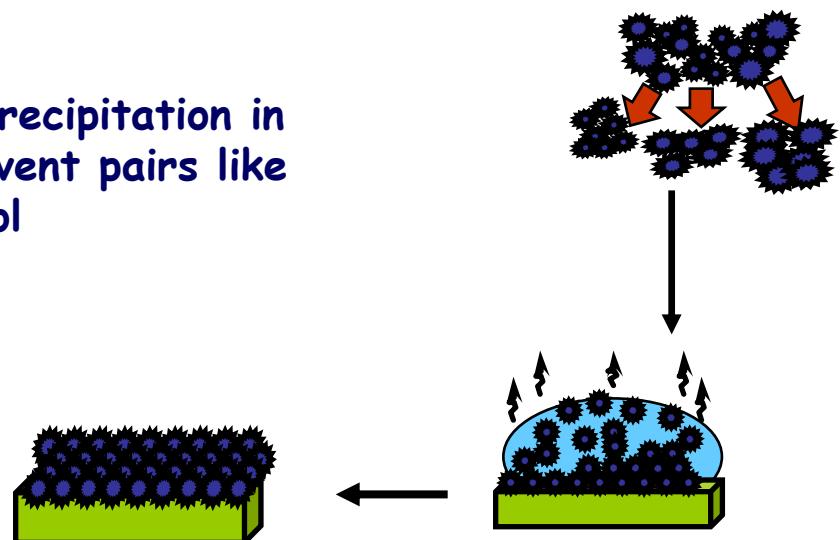


Size Selective Processing

Size selective precipitation in solvent/ non solvent pairs like hexane-methanol

Self Assembly

Evaporation of the solvent

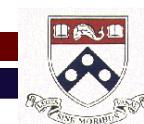
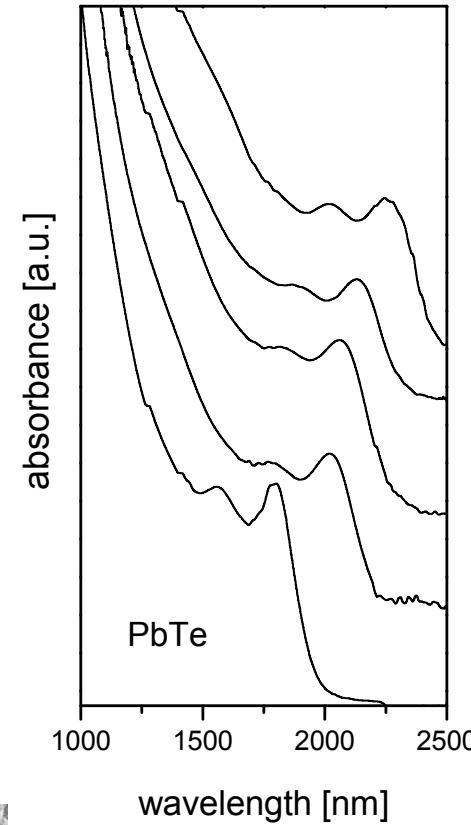
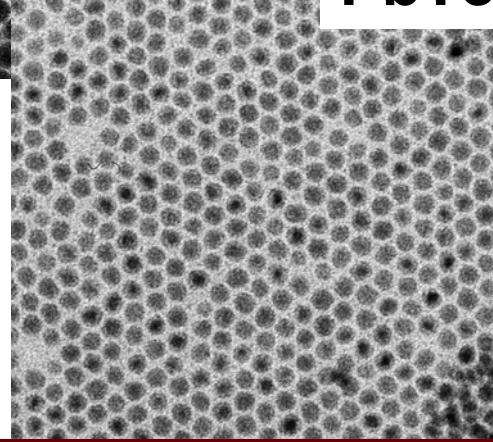
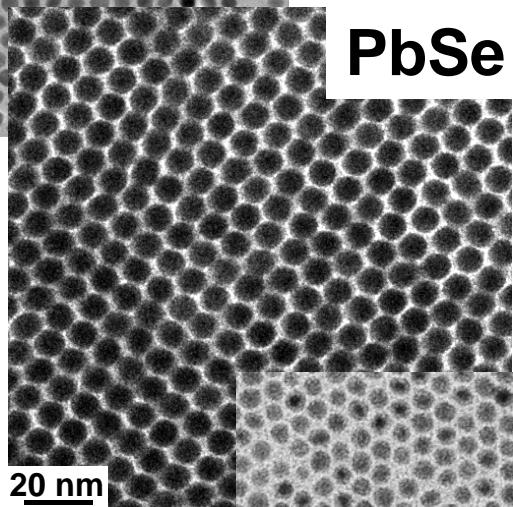
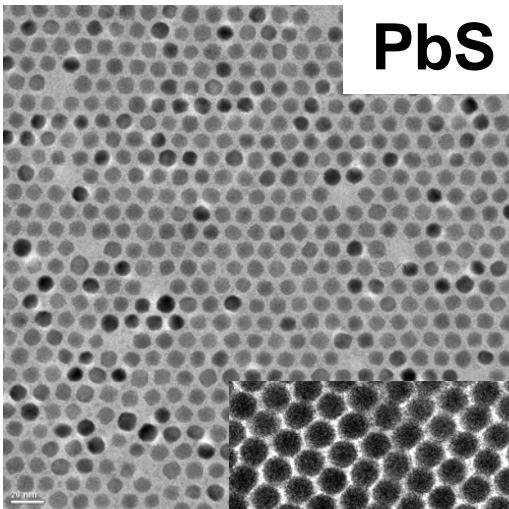
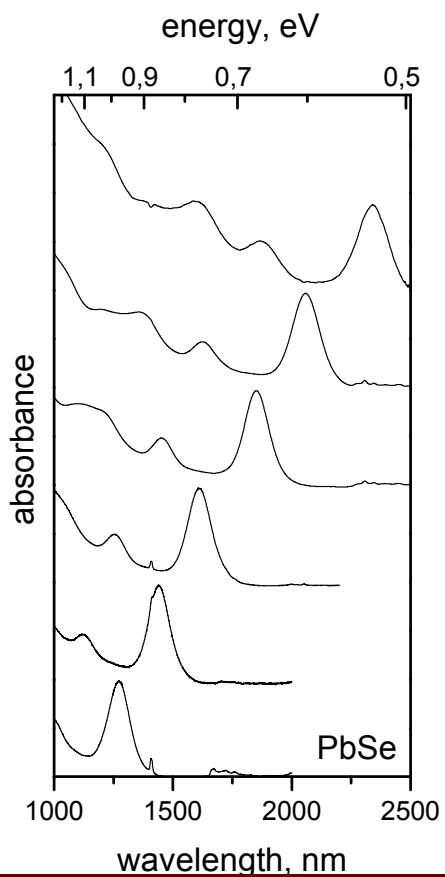


C. B. Murray, S. H. Sun, W. Gaschler, H. Doyle, R. A. Betley, C. R. Kagan IBM J Res Dev 45, 47 (2001)



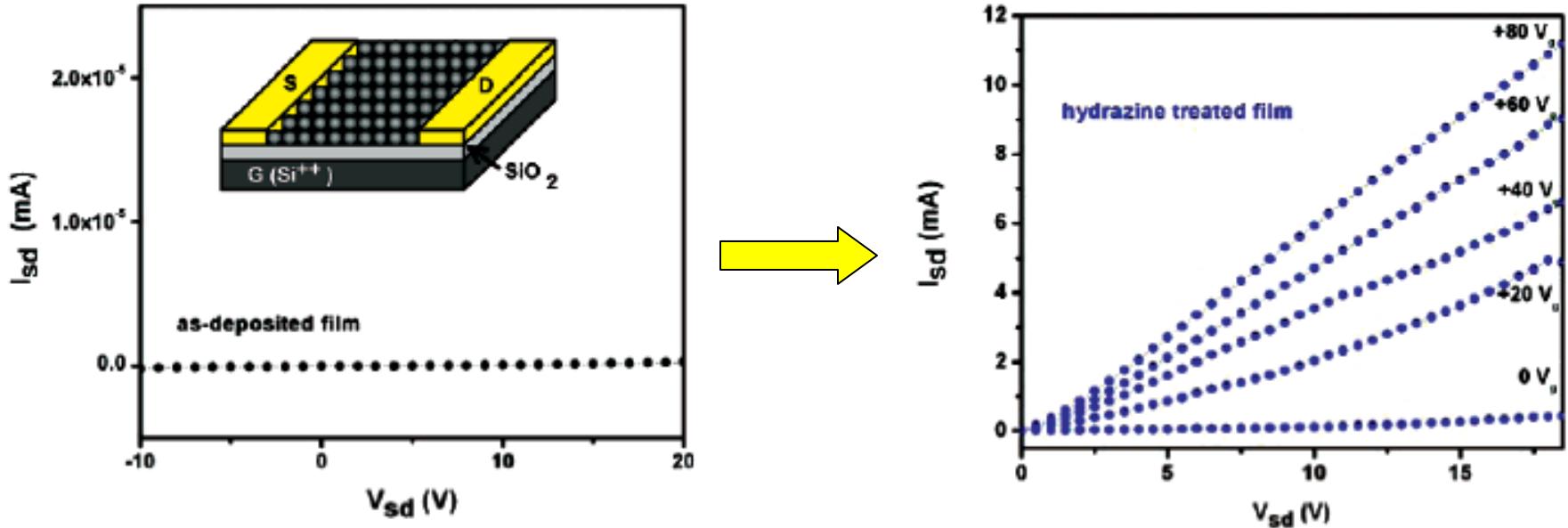
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PbS, PbSe, PbTe Nanocrystals



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Nanocrystal Field-Effect Transistors



Mobility: PbSe $0.95 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$

PbS $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$

PbTe $0.9 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$

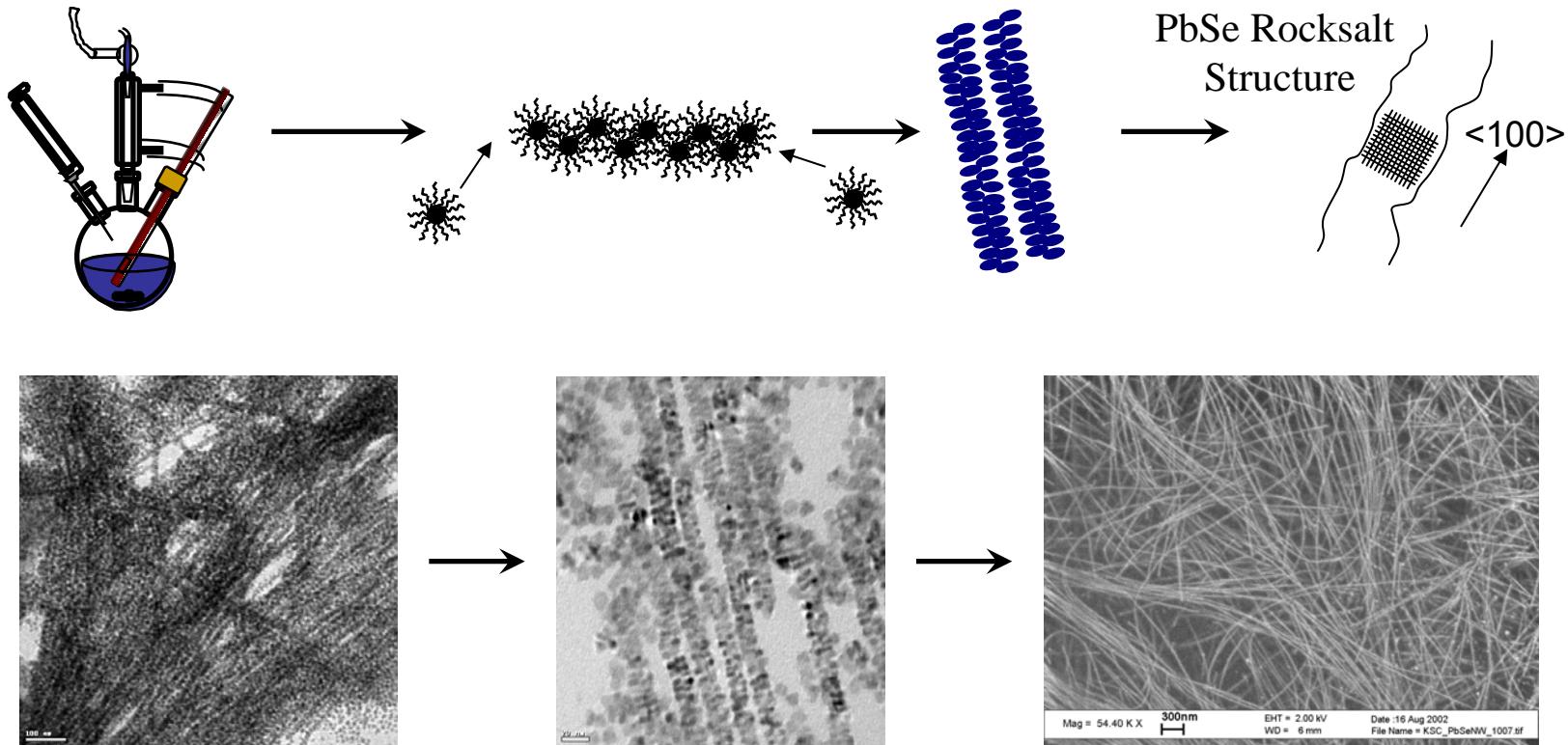
D. V. Talapin & C. B. Murray. *Science* **310**, 86 (2005).

J. J. Urban, D. V. Talapin, E. V. Shevchenko, C. R. Kagan, C. B. Murray, *Nature Materials*, **6**, 115 (2007).



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PbSe Nanowires

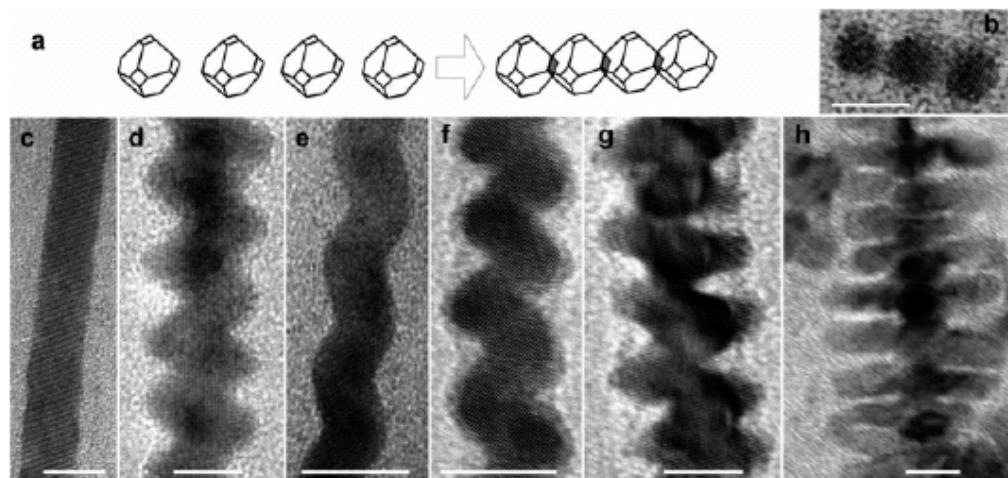


K. S. Cho, D. V. Talapin, W. Gaschler, J. Am. Chem. Soc. **127** 7140 (2005)



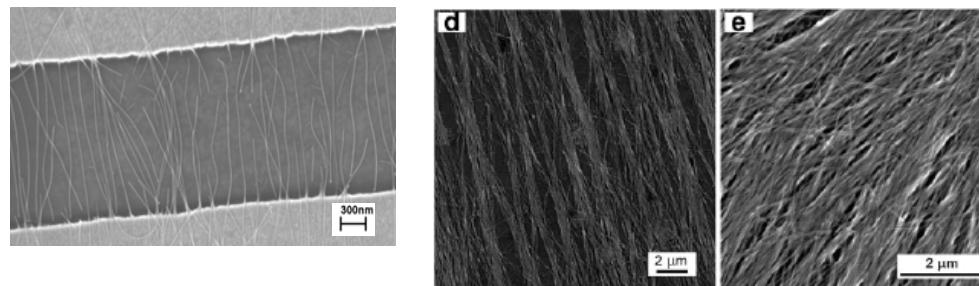
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Wet-Chemical Synthesis of Semiconductor Nanowires



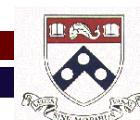
Scale bar is 10 nm

Shape and Size Tunable PbSe
Semiconductor Nanowires



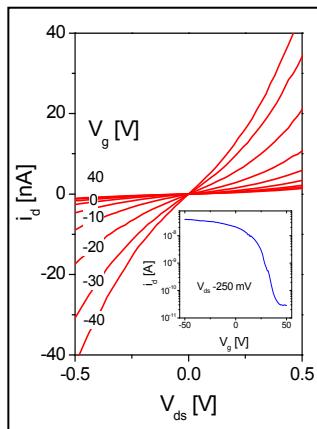
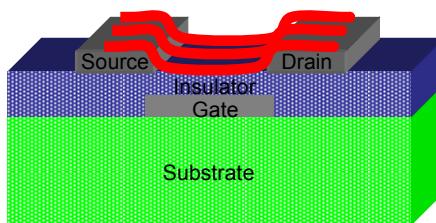
Field-Aligned PbSe
Semiconductor Nanowires

D. V. Talapin, C. T. Black, C. R. Kagan, E. V. Shevchenko, A. Afzali, C. B. Murray, J. Phys. Chem. C, 111, 13244 (2007).

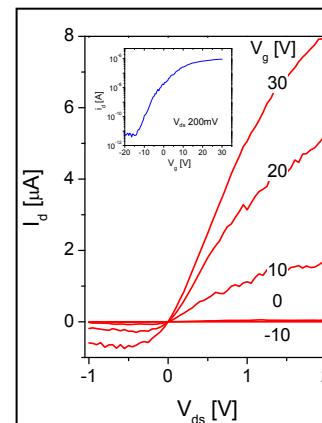


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Charge Transfer Doping of Semiconductor Nanowires



n-dope
with N_2H_4



Hydrazine (a Lewis Base)
replaces bulky oleic acid at NC surface
reduces oxidized surface sites
electron donor: passivates surface traps and dangling bonds
n-type charge transfer doping

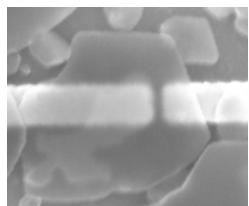


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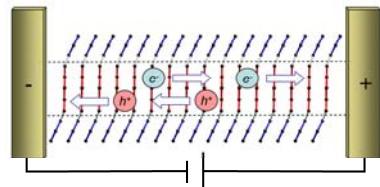
Collaborators



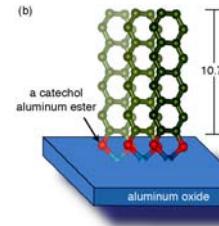
Ali Afzali
Terri Graham



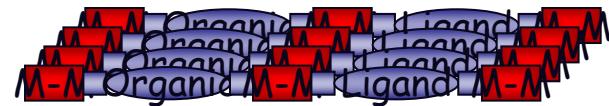
George Tulevski (Columbia)
Qian Miao (Columbia)
Colin Nuckolls (Columbia)



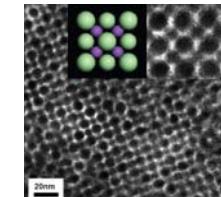
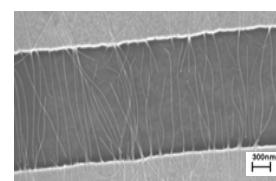
Yaron Cohen (NSEC bridging postdoc)
S. Xiao (Columbia)
Mike Steigerwald (Columbia)
Colin Nuckolls (Columbia)



George Tulevski (NSEC bridging student)
Qian Miao (Columbia)
Colin Nuckolls (Columbia)
Masafumi Fukuto (BNL)
Ben Ocko (BNL)
Ron Pindak (BNL)



Chun Lin (postdoc, UDT)
Libor Vyklicky (postdoc, IBM)



Dimitri Talapin
Jeff Urban
Elena Schevchenko
Chris Murray
Chuck Black